

1,144,497



## PATENT SPECIFICATION

NO DRAWINGS

1,144,497

Inventors: KENNETH HUGH BOURNE,  
KENNETH WALTER ARTHUR CHATFIELD  
and CHRISTOPHER JOHN LEONARD METCALFE

Date of filing Complete Specification: 18 May, 1966.

Application Date: 30 Sept., 1965.

No. 4538/65.

Complete Specification Published: 5 March, 1967.

© Crown Copyright 1969.

11  
11

## ERRATUM

SPECIFICATION No. 1,144,497

Page 1, Heading, Application Date: for "No.  
4538/65" read "No. 41538/65"

THE PATENT OFFICE  
28th April 1969

45

50

It is known that elemental nickel will take up sulphur from hydrocarbon feedstocks under appropriate conditions. Depending on the type of sulphur compound present and the conditions used the sulphiding of the nickel may be partial or may continue until the nickel is converted wholly to nickel sulphide. Catalysis of nickel on a refractory support are also well-known, the support serving to disperse the nickel and increase the amount of surface readily available to the reactants.

The present invention is concerned with the use of a particular supported nickel contact material which has the nickel in finely dispersed form.

According to the present invention a process for desulphurising hydrocarbon feedstocks comprises passing a hydrocarbon feedstock containing admixed sulphur compounds over a contact material comprising elemental nickel on a refractory inorganic oxide support of an element of Groups II, III or IV of the Periodic under conditions such that sulphur is taken up by the nickel without appreciable conversion of the hydrocarbons, said contact material having been prepared by a technique of ion exchange, as hereinafter defined followed by reduction of ionic nickel to elemental nickel.

The sulphur compounds associated with hydrocarbons are usually organic sulphur com-

The sulphur content of the feedstock is not critical, and may be in the range from 0.5 parts per million to 1% wt. Clearly, however, with high sulphur contents the nickel will be more rapidly sulphided and require more frequent replacement or regeneration. Because of this the process is particularly suitable for use with hydrocarbon feedstocks which contain from 0.5 to 100 parts per million of sulphur, more particularly 0.5 to 10 parts per million. While conventional hydrocatalytic desulphurisation may desulphurise hydrocarbon feedstocks to quite low levels, it does not easily remove the last traces of sulphur, particularly if the sulphur is thiophenic, hence the particular suitability of the present process for low sulphur feedstocks.

The hydrocarbons may be of any type, being either saturated, such as acyclic paraffins and naphthenes, or unsaturated such as aromatics and olefins. Examples of suitable feedstocks are those boiling up to 250°C, particularly those containing from 1 to 100% wt of aromatics. Thus the feedstocks may be benzene derived from either oil or coal or petroleum fractions boiling up to 250°C.

While desulphurisation may theoretically occur in the absence of hydrogen, it has been found that the presence of hydrogen is beneficial, due it is believed to the desirability of hydrogenating the unsaturated hydrocarbon

55

60

65

70

75

80

85

BEST AVAILABLE COPY

1144497



# PATENT SPECIFICATION

NO DRAWINGS

1144497

Inventors: KENNETH HUGH BOURNE,  
KENNETH WALTER ARTHUR CHATER  
and CHRISTOPHER JOHN LEONARD METCALFE

Date of filing Complete Specification: 18 May, 1966.

Application Date: 30 Sept., 1965.

No. 4538/65.

Complete Specification Published: 5 March, 1969.

© Crown Copyright 1969.

Index at acceptance:—C5 E12C; C1 A(13, N4B, N48A)

Int. Cl.:—C10 g 23/02

## COMPLETE SPECIFICATION

### Improvements relating to the Desulphurisation of Hydrocarbon Feedstocks

5 We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Flinsbury Circus, London, E.C.2, England, a company incorporated in accordance with the Laws of England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described and by the following statement:—

10 This invention relates to the desulphurisation of hydrocarbon feedstocks without appreciable conversion of the hydrocarbons.

15 It is known that elemental nickel will take up sulphur from hydrocarbon feedstocks under appropriate conditions. Depending on the type of sulphur compound present and the conditions used the sulphiding of the nickel may be partial or may continue until the nickel is converted wholly to nickel sulphide. Catalysts 20 of nickel on a refractory support are also well-known, the support serving to disperse the nickel and increase the amount of surface readily available to the reactants.

25 The present invention is concerned with the use of a particular supported nickel contact material which has the nickel in finely dispersed form.

30 According to the present invention a process for desulphurising hydrocarbon feedstocks comprises passing a hydrocarbon feedstock containing admixed sulphur compounds over a contact material comprising elemental nickel on a refractory inorganic oxide support of an element of Groups II, III or IV of the 35 Periodic under conditions such that sulphur is taken up by the nickel without appreciable conversion of the hydrocarbons, said contact material having been prepared by a technique of ion exchange, as hereinafter defined followed by reduction of ionic nickel to elemental nickel.

40 The sulphur compounds associated with hydrocarbons are usually organic sulphur com-

pounds but free sulphur or hydrogen sulphide may sometimes be present. Feedstocks contain- 45 ing any type of organic sulphur compound or hydrogen sulphide may be treated, since the catalyst has shown its ability to desulphurise feedstocks containing a ring type sulphur compound, thiophene, which is generally 50 acknowledged to be the most stable type of sulphur compound and the most difficult to desulphurise. The present invention is, in fact, particularly suitable for the removal of thiophenic sulphur from hydrocarbon feedstocks. 55 The sulphur content of the feedstock is not critical, and may be in the range from 0.5 parts per million to 1% wt. Clearly, however, with high sulphur contents the nickel will be more rapidly sulphided and require more frequent 60 replacement or regeneration. Because of this the process is particularly suitable for use with hydrocarbon feedstocks which contain from 0.5 to 100 parts per million of sulphur, more particularly 0.5 to 10 parts per million. While 65 conventional hydrocatalytic desulphurisation may desulphurise hydrocarbon feedstocks to quite low levels, it does not easily remove the last traces of sulphur, particularly if the sulphur is thiophenic, hence the particular suitability of the present process for low sulphur 70 feedstocks.

The hydrocarbons may be of any type, being either saturated, such as acyclic paraffins and naphthenes, or unsaturated such as aromatics 75 and olefins. Examples of suitable feedstocks are those boiling up to 250°C, particularly those containing from 1 to 100% wt of aromatics. Thus the feedstocks may be benzene derived from either oil or coal or petroleum 80 fractions boiling up to 250°C.

While desulphurisation may theoretically occur in the absence of hydrogen, it has been found that the presence of hydrogen is beneficial, due it is believed to the desirability of 85 hydrogenating the unsaturated hydrocarbon

[Price 4s. 6d.]

SEE APPROPRIATE SLIP ATTACHED

- radicals liberated from the sulphur compounds when the sulphur is taken up by the nickel. With hydrogen present and with feedstocks originally containing unsaturated hydrocarbons, therefore, precautions may have to be taken to prevent hydrogenation of the unsaturates, for example by limiting the temperature, pressure, or hydrogen partial pressure. Ways of controlling hydrogenation in desulphurisation processes using nickel are described in the specifications of British Patent Applications Nos. 28768/65 (Serial No. 1,144,496), 41940/65 (Serial No. 1,141,809) and 41941/65 (Serial No. 1,144,498). Nickel and sulphided nickel are also known to act as hydrocracking catalysts at temperatures of 250°C or higher, so care should also be taken to prevent this form of hydrocarbon conversion during desulphurisation. Control of temperature and/or the amount of hydrogen present are particularly suitable means of limiting cracking. Suitable conditions for desulphurisation may thus be chosen from the following ranges

|   |            |
|---|------------|
| Temperature °C.                                 | 50 to 300  |
| Pressure psig                                   | 0 to 500   |
| Hydrocarbon liquid hourly space velocity v/v/hr | 0.1 to 10  |
| Hydrogen : hydrocarbon mole ratio               | 0 to 5 : 1 |

- The term "without appreciable conversion of the hydrocarbons" as used in the present specification means that not more than 10% wt. and preferably not more than 5% wt. of the feedstock is converted.
- The catalyst used is, as stated earlier, prepared by an ion exchange technique followed by reduction of ionic nickel to elemental nickel. "Ion exchange" means the replacement of hydrogen atoms in the original oxide by metal cations so that the metal is chemically combined with the oxide and not merely admixed with the oxide. Although pure inorganic oxides do not contain hydrogen, in practice oxides suitable for use as catalyst supports and prepared by calcination at temperatures up to 500°C do contain a small amount of hydrogen, possibly as hydroxyl groups on the surface of the oxide.
- A particularly suitable technique of ion-exchange is described in U.K. Application 22976/65 (Serial No. 1,144,494) involving contacting a refractory inorganic oxide of an element of Group II, III or IV of the Periodic Table containing hydrogen atoms with an aqueous alkaline solution so that the hydrogen is exchanged for alkaline cations, simultaneously or subsequently contacting the oxide with a solution containing cations of a metal of Group I(b), II(b), IV(b), V(b), VI, VII or VIII of the Periodic Table so that the alkaline cations are exchanged for metal cations, thereafter washing with water to remove substantially all the chemically uncombined alkali and metal cations and drying the composite so formed.
- The refractory inorganic oxide may be a single oxide or a mixture of oxides. The preferred hydrogen-containing oxides are those which do not have strong protons, since it has been found that such oxides cannot be directly ion exchanged with a metal without an intermediate treatment. Preferred oxides are alumina, magnesia and, particularly, silica.
- Since oxides can differ appreciably in the number and strength of the protons they carry, experiment may be necessary to determine which oxides are suitable for use in the present invention. Such experiment however, can be simple and quick. Thus the presence of hydrogen can readily be determined by a preliminary treatment with an alkaline solution followed by a water wash and analysis of the oxide for retained alkali. Similarly the strength of the protons can be tested by treating the oxide with a solution containing metal cations, without a previous alkali treatment, washing and analysing to see if the metal cations have been retained. If they are not retained in substantial amount then a preliminary treatment with alkaline solution is desirable.
- The refractory inorganic oxide is prepared prior to treatment according to the present invention. Preparation of an oxide normally involves formation of a hydroxide, drying of the hydroxide to remove excess water and finally calcination of the hydroxide to the oxide. The term "refractory oxide support" includes the dried hydroxide as well as the calcined oxide, but excludes the so called hydrogels or hydrosols containing excess water. The oxide may be formed into particles of a suitable size and shape at any convenient point in the preparation of the catalyst, but preferably before the treatment of the oxide by ion exchange.
- The oxide may be washed with water prior to the treatment with the aqueous alkaline solution to remove any loosely-held impurities and to wet the oxide.
- An essential requirement of the preparation is the washing with water after impregnation

to remove uncombined metal cations. This washing must be carried out while the metal cations are still in a water-soluble state (i.e. before any decomposition or calcination step which would convert uncombined metal cations to a water insoluble state). This washing step distinguishes the process from the conventional impregnation technique in which a decomposition or calcination step follows on the impregnation without an intermediate water wash.

The oxide may, if desired, contact the solutions used by being immersed in them, preferably for a period of 15 minutes to 24 hours. Alternatively, one may percolate the solutions through a bed of oxide particles. This alternative technique provides a further distinction over impregnation techniques in which immersion is usual.

The aqueous alkaline treatment in terms of strength of alkali and contact time should clearly not be such as to destroy the oxide structure itself.

Preferably the treatments with the solutions are carried out successively. Slightly different techniques will be required depending on whether the treatments are simultaneous or successive.

With successive treatments, the alkaline solutions may be derived from the alkali metals of Group I, but the preferred solution is aqueous ammonia. However, solutions of sodium hydroxide may be used and also solutions of salts of weak acids and strong bases for example sodium salts of weak acids, particularly sodium bicarbonate. The total amount of alkali used will depend on the number of protons in the original oxide which can be exchanged for alkaline cations, and this can, if necessary, be determined by a preliminary experiment. Usually an amount of alkali in excess of the amount theoretically required will be used to ensure rapid and efficient exchange of hydrogen by the alkaline cation. Preferably the total amount of alkali used will be up to 20% wt by weight of oxide. The temperature of the treatment is conveniently ambient temperature, although elevated temperatures may be used if desired.

With successive treatments the oxide may be washed with water after the treatment with the aqueous alkaline solution to remove excess alkali which has not exchanged with the hydrogen of the oxide.

The washing should be continued until the pH of the washing eluent is below the pH at which the nickel salt subsequently used forms hydroxides, since if this pH is not reached the metal may be precipitated. The pH at which nickel forms hydroxides is 7.7.

The oxide containing alkaline cations is then treated with a solution containing nickel cations. The solutions are preferably solutions of nickel salts, for example nickel nitrate, chloride, or sulphate. The amount of nickel cation used will depend on the number of

alkaline cations on the oxide, which, as explained above, depends on the original oxide and the same general considerations apply as for the treatment with the alkaline solution. Again the temperature may conveniently be ambient, although elevated temperatures are not excluded.

After the addition of the nickel cations the composite so formed is, as stated above, washed with water to remove substantially all the chemically uncombined cations. Anions will also be removed when a salt solution has been used. The composite is then dried to remove water, preferably at 100—120°C.

The water used for washing is desirably free from ions other than those already present on the composite and initially, therefore, de-ionised water may be used. Removal of substantially all metal cations not chemically bound to the support will occur when the washing is continued until no further cations are removed from the catalyst. This can readily be determined by analysis of the effluent from the washing. Other conditions for the washing are not critical, affecting only the speed of the catalyst preparation rather than the final result. Suitably the temperature may be in the range 15°C to the boiling point of water at the pressure used, preferably 15 to 100°C. Atmospheric pressure is preferred, but pressures above or below atmospheric are also suitable. The quantity of water used is suitably 2 ml to 100 ml per ml of catalyst and the length of time of the washing may be from 10 minutes to 10 hours.

With simultaneous treatment, the preferred alkaline solution is again aqueous ammonia, and the preferred metals and the quantities used are also as for the successive treatments. Thus a solution of nickel formate in aqueous ammonia is particularly suitable. With the simultaneous treatment, however, it is desirable to wash with the alkaline solution free of metals before the water wash.

The actual amount of nickel on the finished composite will depend on the original oxide used, but, in general, with the known refractory inorganic oxides the amount is likely to be relatively low and within the range 0.1 to 5% wt. With the preferred oxide, silica, the amount may be 0.01—2% wt if sodium is the alkali, and 0.01—4% wt if ammonia is the alkali.

The dried composite has the nickel distributed over the support as individual cations or in small aggregations only and these nickel cations have then to be reduced to elemental metal. When so reduced the metal is in a very fine state of sub-division with a high ratio of metal surface to total metal. This fine state of sub-division is believed to give significant advantages in use over composites prepared by conventional impregnation techniques and allows the use of lower total amounts of metal to obtain a given effect.

However, it has been found that ion-exchanged composites are not readily reduced by a simple treatment with hydrogen and, accordingly, the nickel is reduced to elemental metal by removing combined water associated with the metal cations and heating the inorganic oxide containing the metal cations in a reducing atmosphere.

It is thus postulated that the difficulty of reducing ion-exchanged cations is the result of association of combined water with the metal cations. This water is not removed by the simple conventional drying of the catalyst at temperatures of 100–120°C. More severe treatment is required to remove this water and particular techniques that have been found to be suitable are:

- (a) heating in a reducing atmosphere at a temperature of at least 350°C and preferably at least 500°C,
- (b) heating in a stream of an inert gas, such as nitrogen,
- (c) displacement of the water by treatment with a hydrocarbon.

In method (a) the removal of water and the reduction occur together, but the method has the disadvantage that high temperatures of at least 350°C, preferably at least 500°C are required. In method (b) the water is removed in a separate step before the reduction, and this allows the subsequent reduction to occur more readily at lower temperatures. In method (c) the reduction may be simultaneous with or subsequent to the water removal, and in either case, the reduction can be carried out at lower temperatures if desired.

In method (a), the upper limit of temperature will be fixed by the temperature at which the inorganic oxide is likely to be damaged by, for example, loss of surface area or conversion to a less desirable crystalline form, such, as in the case of alumina, alpha-alumina. A convenient practical upper limit for most inorganic oxides is 900°C.

Increased time increases the extent of reduction and the time may conveniently be in the range 3 to 50 hours.

Suitable treatments with an inert gas, method (b), may be at temperatures of from 300 to 600°C for 3 to 30 hours, less time being required at the higher temperatures.

Suitable displacement techniques, method (c), may be contact with a hydrocarbon, particularly an unsaturated hydrocarbon, for example isoprene, at temperatures of 250–400°C for 3 to 8 hours.

For treatments of the (b) and (c) type the reduction may be carried out at temperatures of from 250 to 600°C, preferably 250–400°C, for 3 to 30 hours.

A convenient reducing atmosphere for all the methods is an atmosphere of hydrogen, which may if desired be static, but which is preferably a flowing stream of hydrogen.

The fact that water is associated with the metal cations and that this is responsible for the difficulty of reducing the cations is shown by the evolution of water and by a change in the ultra violet absorption spectrum of the cations during the heating. The change in the spectrum indicated, in the case of nickel ions, that the environment of the nickel ions passed from hexaquo octahedral divalent nickel to mixed oxyaquo octahedral divalent nickel. Thus water is removed from the nickel co-ordination sphere, which then becomes associated with the oxygen atoms in the silica lattice.

A convenient way of determining the amount of elemental nickel present is by taking a small sample of the composite and treating it with an acid such as hydrochloric acid and measuring the amount of hydrogen produced. Ionic nickel does not decompose HCl in this way, but instead the nickel ions are exchanged back again to hydrogen.

The invention is illustrated by the following Examples.

#### EXAMPLE 1.

A 500 ml batch of 72–100 mesh silica was contacted with two 750 ml aliquots of saturated sodium bicarbonate solution at room temperature and then washed with four 750 ml aliquots of deionised, distilled water. Nickel was introduced by contacting the washed solid with two 750 ml aliquots of M/10 nickel nitrate solution and surplus salt washed away by eight successive contacts with 750 ml aliquots of water.

Each of the above contacts lasted five minutes and the solid was agitated to ensure efficient exchange or washing. The resultant solid was dried for 16 hours at 110°C; the nickel content was 1.47 per cent wt. After reduction for 4 hours in 1000 v/v/hr of hydrogen at various temperatures the amount of elemental nickel produced was estimated from the amount of hydrogen evolved from a 3 g sample of the catalyst treated with N hydrochloric acid.

| Reduction<br>Temperature<br>°C. | Elemental<br>Ni present<br>% wt. | Percentage of<br>Ni reduced |
|---------------------------------|----------------------------------|-----------------------------|
| 350                             | 0.14                             | 9.55                        |
| 400                             | 0.33                             | 22.4                        |
| 465                             | 0.69                             | 47.0                        |
| 500                             | 1.10                             | 74.9                        |
| 500*                            | 1.28                             | 87.5                        |

\* after 16 hours reduction.

#### EXAMPLE 2.

A reduced nickel-silica composite was prepared by placing 120 ml of 6-12 mesh (BSS) silica in a glass column and percolating one litre of 50% volume 0.8% SG ammonia solution over a period of 5 hours. The silica was washed by percolating one litre of deionised water through the bed overnight. An overnight percolation of one litre of M/2 nickel nitrate solution followed. The bed was washed with deionised water until the wash water was colourless and then exhaustively extracted with water in a Soxhlet apparatus for 8 hours. The silica was dried at 110°C and the nickel ions were reduced to nickel by heating at 500°C for 4 hours in hydrogen. The nickel content was 4.9% wt.

The composite was used to desulphurise benzene containing 21 ppm. of sulphur (as thiophene) at 204°C, 100 psig, 1 v/v/hr and with the amount of hydrogen limited to keep the conversion of benzene to cyclohexane at 13%.

The sulphur content of the benzene was reduced to an average of 0.6 ppm for a period of 220 hours, corresponding to a S:Ni atomic ratio of the composite of 0.23:1 at the end of this period.

#### WHAT WE CLAIM IS:—

1. A process for desulphurising hydrocarbon feedstocks comprising passing a hydrocarbon feedstock containing admixed sulphur compounds over a contact material comprising elemental nickel on a refractory inorganic oxide support of an element of Groups II, III or IV of the Periodic Table under conditions such that sulphur is taken up by the nickel without appreciable conversion of the hydrocarbons, said contact material having been prepared by a technique of ion exchange, as hereinbefore defined, followed by reduction of ionic nickel to elemental nickel.

2. A process as claimed in claim 1 wherein the sulphur content of the feedstock is from 0.5 to 100 ppm by weight.

3. A process as claimed in claim 1 or 2 wherein the sulphur is predominantly thiophenic sulphur.

4. A process as claimed in claim 1, 2 or 3 wherein the hydrocarbon feedstocks boil up to 250°C.

5. A process as claimed in any of claims 1 to 4 wherein the desulphurisation is carried out at a temperature of from 50 to 300°C.

6. A process as claimed in any of claims 1 to 5 wherein the desulphurisation is carried out at a pressure of from 0 to 500 psig, a hydrocarbon space velocity of from 0.1 to 10 v/v/hr and a hydrogen:hydrocarbon mole ratio of from 0 to 5:1.

7. A process as claimed in any of claims 1 to 6 wherein the contact material is prepared by forming a composite of nickel cations and refractory inorganic oxide by an ion-exchange technique, and reducing the ionic nickel to elemental nickel by removing combined water associated with the nickel cations and heating the composite in a reducing atmosphere.

8. A process as claimed in any of claims 1 to 7 wherein the contact material is formed by contacting a refractory inorganic oxide of an element of Group II, III or IV of the Periodic Table containing hydrogen atoms with an aqueous alkaline solution so that the hydrogen is exchanged for alkaline cations, simultaneously or subsequently contacting the oxide with a solution containing nickel cations so that the alkaline cations are exchanged for nickel cations, thereafter washing with water to remove substantially all the chemically uncombined alkali and metal cations, drying the composite so formed, and reducing the nickel cations to elemental nickel.

9. A process as claimed in any of claims 1 to 8 wherein the refractory inorganic oxide is silica.

10. A process as claimed in any of claims 1 to 9 wherein the nickel content of the finished composite is from 0.1 to 5% wt.

11. A process as claimed in claim 1 substantially as described in the Examples.

---

J. WOOLARD,  
Agent for the Applicants,  
Chartered Patent Agent.

---

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.  
Published by the Patent Office, 25 Southampton Buildings, London, W.C. 2, from which  
copies may be obtained.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**